CEMENT AND LIME MANUFACTURE

PUBLISHED 20TH OF EACH MONTH. PRICE 1/- A COPY. ANNUAL SUBSCRIPTION 12/- POST FREE.

PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED
14 DARTMOUTH STREET, LONDON S.W.1

TELEPHONE: WHITEHALL 4581
TELEGRAPHIC ADDRESS:
CONCRETIUS PARL. LONDON

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & LIME MANUFACTURE"
"THE CONCRETE YEAR BOOK"
"CONCRETE SERIES" BOOKS, ETC.

VOLUME XI. NUMBER 11 NOVEMBER 1938

The Effect of Water in Concrete.

By GABRIEL A. ASHKENAZI
(BROOKLYN, NEW YORK).

COMMERCIAL Portland cement comprises a heterogeneous system of several ingredients, existing partly in the form of crystalline individuals, partly in the form of solid solutions, and partly as an amorphous glassy substance. The hydration and hardening of cement have been the subjects of comprehensive investigations, but there is still much that is unintelligible in this process. The reasons for this are manifold and in principle well known. A few years ago in this journal[1] Messrs. W. Watson and Q. L. Craddock gave a detailed account of the research on the hydration, setting, and hardening of Portland cement. The explanations of the hardening of cement are based on the colloid and the crystal theories. Most investigators consider the process of setting and hardening to be a result of colloid and crystal formation. The fact that the first reaction of cement on hydration results in the formation of colloids is indisputable. That, however, does not exclude the possibility that in time the colloid mass may be converted into metacolloidal, or even ultramicro-crystalline, form. Attempts to discover crystals in thin sections of set cement have failed. According to Professor Kühl[2], thin sections, even twenty years old, did not show the presence of crystals.

The hardening of concrete can be better understood and explained if we accept the colloid theory. The first action of water on cement hydrolyses the constituents and produces colloidal solutions which form gels. The cement gels are characterised by their tendency to absorb a considerable amount of water; the ability to absorb varying amounts of liquid is a characteristic property of all the colloids. J. M. Van Bemmelen[3] proved that silica forms hydrogels containing as many as 331 mol. of absorbed water per molecule of silica. Cement gels, composed chiefly of calcium hydro-silicates, absorb a certain amount of water which can

vary considerably depending on different conditions, but obviously there is a maximum which can be retained depending upon the chemical and granular composition of cement, the temperature, and the atmospheric humidity. The proportion of water in gel affects its cohesive properties, and accordingly the strength of concrete. Tests of bond resistance and compression carried out by Duff A. Abrams[4] on specimens of concrete caused to set under pressure, proved that an excess of water could be expelled and the strength of concrete increased by 90 per cent. In practice, when mixing concrete, an amount of water ranging from 50 per cent. to 100 per cent. of the weight of cement is normally used. Part of this water is bound by the formation of hydroxides and hydrates, part is absorbed by gel but part remains as free water in concrete. We do not know exactly what amount of water is actually required by cement in order to produce a resistant cohesive structure. An opinion has been expressed[5] that " the water needed for chemical combinations is about 10 per cent. of the weight of cement, but for the production of gel at least three times as much is needed." This is of course a pure assumption. Anderegg and Hubbell[6] have shown that the finest particle of cement is, after a long period of time, not completely hydrated. They found that the depth of penetration of water into a cement grain, immersed in water for 28 days, does not exceed a few thousandths of a millimetre. Considering the fact that even at the age of 28 days only a small part of the cement in concrete is hydrated, the amount of water actually consumed may be considerably smaller. The process of hydration may go on for a very long time, but normally the bulk of the hardening is produced at early ages and the following development proceeds very slowly. Theoretically this process may go on until each cement grain is finally hydrated, provided there is free water in the concrete and assuming that the colloid gel surrounding the unhydrated part retains its semi-permeable structure and has not become impervious to water. Old cement pats show the presence of unhydrated cement and it has been proved that " cement pats, which have been stored for twenty or even thirty years in water, have the ability again to set and harden when they are reground."[7] Thus the amount of mixing water used in practice greatly exceeds that needed for the hydrolytic decomposition of cement and for the production of gel.

This excess of water in concrete exists chiefly in two forms : as water absorbed in the colloidal cells and as free water filling the cavities in the interior of the concrete. It has already been mentioned that the colloid mass has the ability to absorb a large quantity of water. With respect to the silica hydrogel, it has been shown that the amount of absorbed water influences the resistance of water-charged gel to compression. W. Michaelis, Jr.[8] proved that these hydrogels, after being dried by means of water-absorbent agents and then compressed into a cake, show resistances to compression which decrease with the increase of the amount of water remaining in the hydrogel. For example, silica hydrogel dried to a water content of 100 per cent. showed a resistance of 1200 lb. per square inch ; hydrogel with a water content of 45 per cent., about 9030 lb. per square inch ; and hydrogel with 16 per cent. water content, about 13980 lb. per square inch.

A similar relationship obviously exists between the strength of cement gel and the proportion of absorbed water. As has been established by Abrams,[9] the development of strength is faster in concrete made with less mixing water ; thus, a mix with a water-cement-ratio of 0·70 develops at seven days the same strength as a mix with a water-cement-ratio of 1·00 at 90 days.[9]

A very wet mix produces an over-expanded gel diluted with water. In time, however, if the curing conditions are favourable, the formation of more gel from the unhydrated part of cement and the loss of water due to the slow natural evaporation make the concrete denser and stronger. The curing conditions in practice are usually far less favourable than those in the laboratory tests. Under the influence of the temperature and atmospheric humidity the process of desiccation may proceed fast and in bounds, accompanied by a sudden shrinkage. The weak colloid mass cannot withstand the stress caused by this shrinkage and the insufficiently jellified cell cracks ; a part of the colloid water is expelled by pressure, thus resulting in a break of continuity in the process of gradual hydration and hardening. In some cases, however, the disturbed process may be restored. Generally, gels show a reversible property of shrinking while drying and swelling on wetting.

As to the silica gel this rule cannot be accepted without reservation. If silica gel is dried sufficiently its power to absorb water and to swell is considerably reduced, or even lost. The same, in a greater degree, is true of the cement gel, but if the cement gel has not yet reached this irreversible state, and it comes in contact with water, it may swell again and refill the existing cracks. If the unhydrated part of cement is not covered by a water-impermeable skin of dried metacolloidal mass, preventing contact with water, new colloid may be produced (self-healing). Such a revival of binding strength may occur, but even then the secondary produced cohesive mass would not develop normal strength. Most likely, however, the dried out gel-cell would remain ungenerated, forming weak points in concrete easily subjected to injurious attacks by different agents.

When the desiccation of an over-expanded gel proceeds normally, the water evaporating from the gel-cells enriches the content of so called " free water " in concrete. Our conception of concrete is still somewhat obscure, but the latest views suggest that concrete does not present a solid stone-like structure. It consists rather of a network of interstices, more or less capillary, containing water and air. This net separates into many parts the really solid ingredients of concrete which form its skeleton. However, this skeleton also contains voids which cannot be avoided in the most carefully prepared concrete. It is well known that even a mortar made of neat cement contains a considerable amount of voids, which increases with the increase of the proportion of mixing water. John R. Baylis[10] found that " voids in neat cement mortar may be varied quite widely according to the quantity of water used in mixing : they range from a minimum of 22 per cent. of the volume with 20 per cent. by weight of water to a maximum of 49 per cent. with 70 per cent. of water."

It has been suggested that carbon dioxide of the atmosphere diffuses through

the capillaries in the mass of concrete, transforming calcium hydroxide, released during the hydration of cement, into calcium carbonate. The latter is practically insoluble in water and, unlike calcium hydroxide, cannot be washed out from concrete. It fills the existing capillaries, reducing the amount of pores and hindering the evaporation of colloidal water. The gel-containing cells retain their elastic semi-permeable structure for a longer period of time and the further gradual hydration of cement is promoted. Such a process of solidification is possible in concrete made of a relatively dry mix, where the greater part of the water has been consumed by chemical combination or is firmly held in the dense, not over-expanded, gel-cell.

Many attempts have been made to determine the proportions of different kinds of water in concrete. Various methods, such as drying, extraction, and freezing have been applied. The results are open to some objections and do not allow an exact conclusion to be drawn. It is especially difficult to make a sharp distinction between the mechanically bound (free water) and the water held by the colloidal mass. The investigations by S. Giertz-Hedstrom,[11] based on separating free water from bound water by freezing, which had been accepted also with some criticism, give indications as to the distribution of water in set cement. According to these tests, specimens made of cement mixed with 26.8 per cent. of water and stored for 28 days in air of 99 per cent. humidity did not show the presence of free water, while others mixed with 49·2 per cent. of water contained, under the same conditions, 9·8 per cent. of free water. Over-wet mixtures with 94·7 per cent. of water contained as much as 54·5 per cent. of mechanically-suspended free water. Due to the influence of alkalis in cement, the amount of free water determined by the freezing method is rather smaller than that really existing.

The distribution of water in concrete made of a relatively dry mix favours the solidifying action of carbon dioxide. Quite a different picture may be drawn if the concrete has been made of a wet, or over-wet, mix. The amount of pores is greatly increased, the over-expanded gel-cells hold their water very loosely, and all the capillaries and voids are filled with water. Carbon dioxide, diffusing through the capillaries, would dissolve the calcium carbonate produced and the calcium hydroxide precipitated on the walls of the pores and capillaries, and the dissolved compounds might be carried out to the exterior, thus resulting in the enlargement of the capillaries and creating a further opportunity for attack. It is generally agreed that there is a constant movement of free water in concrete. In a dry-mix concrete the speed of this circulation gradually decreases, and after a relatively short time may become very slow. The dissolving action of water containing CO_2 creates new possibilities for the flow of water through the enlarged capillaries to the voids in the mass of concrete. The effects of water movement in concrete affect its durability, because, under the influence of different agents, especially of temperature, the capillary interstices may be filled and emptied, thus producing shrinkage which can result in important deformations.[12] Obviously this movement would occur easier and with more harmful results in a

concrete made with a wet mix. The greater amount of free water taking part in this circulation may also accumulate in larger cavities and expand on freezing.

There are other phenomena which the newest researches attribute to the presence of excess water in concrete. For example, Inge Lyse[13] states that " the phenomenon of segregation of water from the paste is noted in all over-wet mixes." According to some investigators[14] " the major portion of plastic flow is apparently due to seepage of colloid water from the cement gel." Creep is a continuous deformation which occurs in concrete under a sustained load. Seepage is the flow of water from the gel due to applied pressure. The over-expanded gel in wet-mixed concrete favours seepage, even under a light pressure.

The outstanding conclusion is that the use of wet mixes cannot be justified. An opinion has been expressed that many structures made of concrete mixed with an excess of water, which " are apparently in good condition, will be found to be below the safety limit," and the writer agrees with this view. The dangers of over-wet mixes have been frequently emphasised, and are known to every constructor. Nevertheless, in practice an excess of water is frequently used to give greater workability, but this advantage is small when compared with the injurious effects which an excess of mixing water may have on concrete.

REFERENCES

1 " Cement and Cement Manufacture," 8, Jan., 1935.
2 Prof. Dr. H. Kühl, " Cement Chemistry in Theory and Practice," p. 34.
3 J. M. Van Bemmelen, Die Absorption, Dresden, 1910, p. 201.
4 Univ. of Illinois Bull., No. 71, pp. 115–120.
5 R. W. Carlson, Highway Research Board. Proc., 1936, Nov., p. 221.
6 Proc. A.S.T.M., 1929, part 2, pp. 554–564.
7 " Cement Chemistry in Theory and Practice," p. 38.
8 Proc. Assoc. German Portland Cement Manufacturers, 1908, p. 83.
9 Am. Conc. Inst. Proc., 27, 1931, p. 1330.
10 Proc. Am. Soc. Civ. Eng., 1906, April, p. 562.
11 Teknisk Tidskrift, 1930, Eng. Abstr., 1931, April, pp. 27–28.
12 E. Freyssinet, " Une revolution dans la technique du beton." Mem. Soc. Ing. Civ. de France, 1935, p. 643–674.
13 Franklin Inst. Journ., 1936, April, p. 498.
14 R. E. Davis, H. E. Davis, and J. S. Hamilton, Proc. A.S.T.M., 34, part 2, p. 354.

Cement Silos and Slurry Tanks.

UNUSUAL DESIGN.

THE cement silos, slurry tanks and washmill for the new works of Eastwood's Humber Cement, Ltd., at South Ferriby, were designed and constructed by Messrs. Christiani & Nielsen, Ltd., under the supervision of Messrs. Horace Boot & Partners, Ltd., consulting engineers. Each of the five slurry tanks is

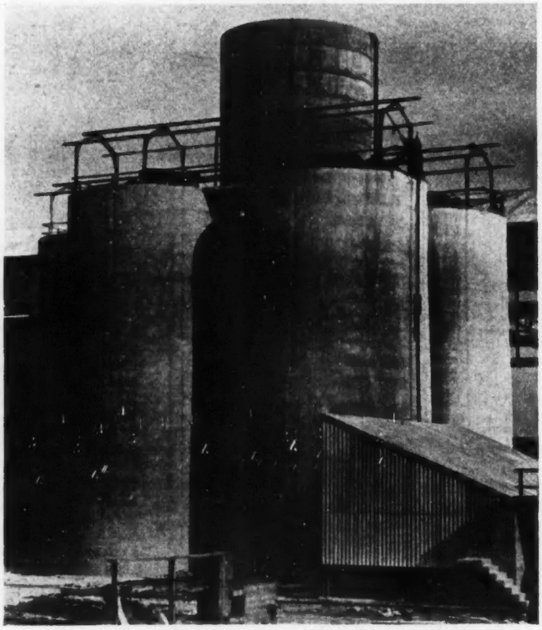

Fig. 1.

23ft. in diameter inside and 52ft. 6in. high ; situated among four of these tanks and surmounting them is an elevated water tank of 50,000 gallons capacity.

In designing the slurry tanks allowance was made for a pressure corresponding to that of a liquid with a specific gravity of 1.6. To resist the ring tension set up by this pressure it was necessary to make the wall 20in. thick at the base, tapering externally to a thickness of 5in. at the top.

The design of the cement silos was also unusual. Of these, two have an external diameter of 33ft. 8in. and four an external diameter of 20ft. ; they all rise to 71ft. 9in. above the ground. Under the system of conveying the cement pneumatically the contents of the silos are agitated with air, thus destroying

all friction of the material within itself or against the walls, and producing a full liquid pressure on the walls and bottom, which is numerically equivalent to its density and assumed to be 75 lb. per square foot. The high ring tension produced by these conditions made it advisable to make the wall thickness in the 33ft. 8in. diameter silos 15in. at the bottom to prevent cracks forming. The wall, for economical considerations, is tapered internally to 5in. at the top.

A comparison of the ring tension produced in the wall of a silo containing cement under normal conditions where friction may be taken into account, and

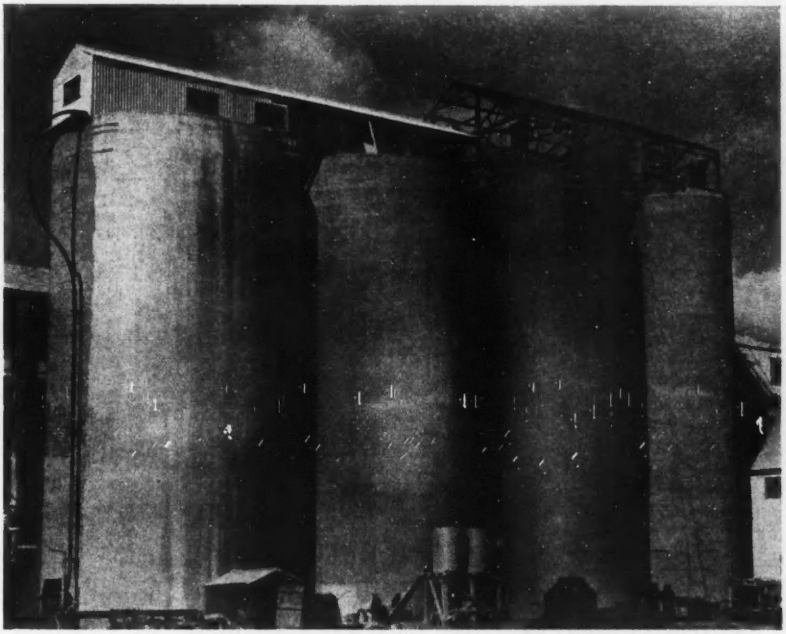

Fig. 2.

in a case such as the present wheie no friction may be allowed, is of interest. In this comparison the following values are used :

Density of normal cement, 90 lb. per cubic foot ;

Density of pneumatically-agitated cement, 75 lb. per cubic foot ;

Angle of repose, $\phi = 18$ deg. ;

Angle of friction against wall, $\phi_1 = 29$ deg. ;

Depth of cement considered, 56ft. ;

Diameter of silo, 32ft.

Using Janssen's formula,

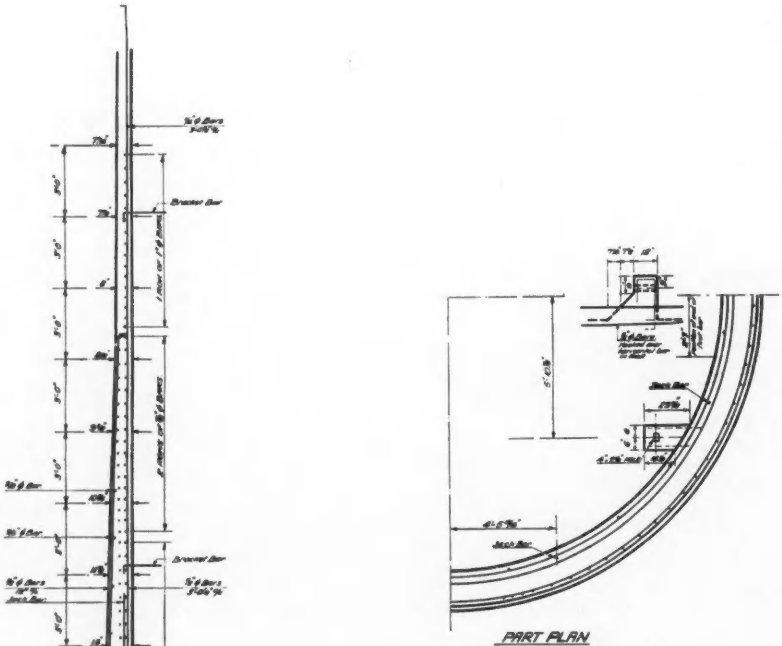
SECTION THRO' WALL
PART PLAN
PLAN OF SLURRY TANKS
Bracket Bar
Jack Bar

Fig. 3.

$$p_h = \frac{wR}{\mu_1}\left(1 - e^{-\frac{k\mu'h}{R}}\right)$$

$$k = \frac{p_h}{p_v} = \frac{1 - \sin\phi}{1 + \sin\phi} = 0.528$$

and $\mu_1 = \tan\ \phi_1 = 0.554$;

$$R = \frac{\text{Area of silo}}{\text{Perimeter}} = \frac{\pi d^2}{4\pi d} = 8\text{ft.}$$

$$\therefore p_h = \frac{90 \times 8}{0.554}\left(1 - e^{-\frac{k\mu'h}{R}}\right).$$

$$= \frac{720}{0.554}\left(1 - e^{\frac{1}{2 \cdot 044}}\right)$$

$= 1130$ lb. per square foot.

The circumferential tension is $1130 \times 16 = 18{,}080$ lb. per foot. For the silos now described, and where no friction is allowed, the circumferential tension is $75 \times 56 \times 16 = 67{,}200$ lb. per foot, or nearly four times as great.

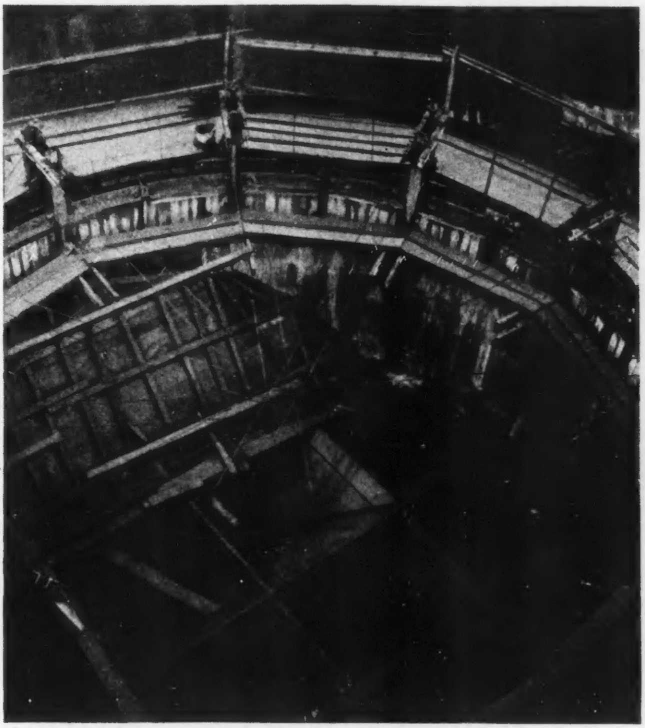

Fig. 4.

For the construction of the slurry tanks and cement silos a special sliding form was adopted which was capable of being decreased in diameter externally in the case of the slurry tanks and increased in diameter internally for the cement silos.

On each of the large cement silos twelve 1-in. diameter jack bars were provided, and on each small silo eight jack bars. Adjustment for obtaining the correct thickness of the walls was made by using circumferential screws placed between the jack bars, and radial screws on the yokes operated simultaneously with the jacks during concreting. The forms were made of timber to the correct radius and circumference at the top of the silos. Allowance for the increase in circumference towards the bottom was made by using a curved metal plate placed between the yokes and attached at its centre to the circumferential adjusting screws, the latter being constructed sufficiently strong to resist the circumferential tension or compression while the concrete was being placed. The metal plates then slide over the timber forms as the screws are adjusted. Owing to a labour shortage work was not carried on by day and night, but continuous jacking and pouring was found to be possible with the tapering sliding forms in practically the same way as with ordinary vertical side sliding forms.

Fig. 1 shows the slurry tanks with external taper to the walls. The uniform internal diameter of these is determined by that of the vanes used to rotate the slurry. *Fig.* 2 shows the group of silos in which the taper is internal. *Fig.* 3 shows the general arrangement of the slurry tanks and the reinforcement details for the bottom of the walls, and a view of the hoppers at the bottom of the large silos during construction is shown in *Fig.* 4.

MISCELLANEOUS ADVERTISEMENTS.

SITUATIONS VACANT.

Phase Equilibria Studies.

Mixtures of the Compounds $4CaO.Al_2O_3.Fe_2O_3—2CaO.Fe_2O_3—K_2O.Al_2O_3$.

By WILLIAM C. TAYLOR.

THE following is an abstract of a paper by Mr. W. C. Taylor (Research Paper R.P. 1131) issued by the United States National Bureau of Standards.

Introduction.

Fundamental thermal studies on various systems of the components of Portland cement have for several years occupied a prominent part in the programme of the Portland Cement Association Fellowship at the National Bureau of Standards. Other workers have made important contributions in this field. Brownmiller and Bogue [1]* presented a comprehensive bibliography in this connection with their paper "The X-ray Method Applied to A Study of the Constitution of Portland Cement." These studies referred to, together with subsequent data obtained by Lea and Parker [2], Dahl [3], and McMurdie and Insley [4], among others, form the basis of the present conception of the constitution of Portland cement with reference to the principal oxides, namely, CaO, SiO_2, Al_2O_3, Fe_2O_3, and MgO.

Of the minor constituents, the alkalis, because of their prevalence, are probably the most important. It was found by the analyses of 23 commercial clinkers that Na_2O and K_2O were both present in all clinkers. The amount of the former varied from 0.1 to 0.7 per cent., and the amount of the latter from 0.1 to 1.6 per cent. The average percentage of each was 0.3 and 0.6 respectively. While these percentages are small, combination of the alkalis with the other constituents may have a significant effect on the ratio of lime to the remaining acidic constituents available.

Accordingly, studies of systems involving the alkalis are being made as a continuation of the series undertaken for the purpose of establishing the constitution of Portland cement clinker. The system $CaO–Na_2O–Al_2O_3$ has been examined by Brownmiller and Bogue [5] and the system $CaO–K_2O–Al_2O_3$ by Brownmiller [6].

It was found that $K_2O.Al_2O_3$ is the only compound of K_2O which is stable at the liquidus in the portion of the $CaO–K_2O–Al_2O_3$ system studied. This means that $K_2O.Al_2O_3$ will crystallise from the melt in all portions of the diagram which were studied. But this does not necessarily mean that $K_2O.Al_2O_3$ exists in Portland cement clinker. Before the manner in which K_2O is combined in clinker can be predicted, thermal studies of systems involving $K_2O.Al_2O_3$ and the silica and the iron compounds of cement are necessary. The present investigation on a portion of the system $CaO–Al_2O_3–Fe_2O_3–K_2O$ is one of such studies.

* Figures in brackets indicate the literature references at the end of the paper.

Experimental Method.

Four series of base compositions were made. In each series the ratio of $4CaO.Al_2O_3.Fe_2O_3$ to $2CaO.Fe_2O_3$ (by weight) was constant but the $K_2O.Al_2O_3$ content varied. The ratios of $4CaO.Al_2O_3.Fe_2O_3$ to $2CaO.Fe_2O_3$ employed were 100 : 0, 90 : 10, 70 : 30, and 50 : 50. The percentage of $K_2O.Al_2O_3$ in the 100 : 0 series varied from 0 to 60, but in the other series from 0 to 25.

In preparing the base compositions, $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.–Fe_2O_3$ were first made independently. These compounds were mixed in the desired proportions and then the Al_2O_3 and K_2O were added separately. Potassium oxalate was used as the source of K_2O since it is not hygroscopic and weighing difficulties are eliminated by its use. After the addition of Al_2O_3 and K_2O the samples were burned at about 1,250 deg. C. for half an hour. The amount of K_2O in the sample was checked by determining the difference in weight before and after burning. Corrections were made when necessary. Potash does not appear to be volatilised rapidly after it has once combined and for that reason combination was first effected by the preliminary burning at temperatures not exceeding 1,250 deg. C.

The small quenching charges were taken from the base samples which had been thoroughly ground after each step in the preparation. These charges were tightly enclosed in platinum foil, the edges of the foil being folded over at least three times. Heating was for as short a time as possible (15 to 20 minutes was found to be ample to bring about equilibrium) in order to avoid loss of potash. The consistency with which various melting temperatures could be checked was accepted as evidence that the loss of K_2O resulting from this procedure was slight.

Very small samples were used because the utmost rapidity is required in quenching. Even so, in samples containing high percentages of the iron compounds, quench growths were found to occur and interpretations had to be made accordingly. In most studies of systems containing Fe_2O_3 the quenching method has heretofore been limited in use because of the rapid crystallisation of the iron compounds. Thermal studies were made with heating curves. However, in the presence of alkalis, thermocouples are readily attacked and for this reason the quenching method is necessary.

The charges were suspended by a very fine platinum wire in the hot zone of a vertical platinum-rhodium resistance furnace. Temperatures were measured by means of a platinum platinum-rhodium thermocouple connected with a Leeds and Northup potentiometer. Temperature control was effected by a Robert's regulator [7]. Because of the susceptibility to attack by the potash the thermocouple in use was calibrated frequently by comparison with a standard couple held in reserve, or by checking the melting points of eutectics in the $CaO–Al_2O_3$ system.

The common procedure of thermal study by the quenching method was followed, whereby the appearance of the sample under the petrographic micro-

scope is used as a means for determining the condition of the charge at the temperature of the furnace just prior to the quenching.

The samples containing K_2O were found to be very hygroscopic and extreme precautions were necessary to avoid hydration of the quenches. The agate mortar and pestle with which they were ground had to be heated previously, and the portions to be examined transferred directly and quickly to the microscope slide.

Phase Equilibria.

The System $4CaO.Al_2O_3.Fe_2O_3$-$K_2O.Al_2O_3$.—Only compositions within the range from 100 per cent. of $4CaO.Al_2O_3.Fe_2O_3$ to 60 per cent. of $4CaO.Al_2O_3$.—Fe_2O_3 and 40 per cent. of $K_2O.Al_2O_3$ were investigated. In regions high in $K_2O.Al_2O_3$ complete melting of the charges occurs only at very high tempera-

TABLE 1.—Thermal Data Relative to the System C_4AF-KA.

Composition		Temperature of quench	Examination
C_4AF	KA		
Percent	*Percent*	*°C*	
100	0	1,418	Glass; few quench growths.
		1,410	All crystalline.
95	5	1,400	Glass.
		1,391	Very small amount C_4AF; glass.
		1,340	All crystalline.
90	10	1,378	Glass.
		1,370	C_4AF; glass.
		1,348	Do.
		1,340	C_4AF; KA.
85	15	1,364	Glass; very few quench growths.
		1,356	C_4AF; glass.
		1,348	Do.
80	20	1,365	Glass.
		1,360	KA; glass.
		1,343	Very small amount of glass; KA; C_4AF.
75	25	1,520	Glass; only trace of KA.
		1,500	KA; glass
70	30	1,560	Do.
		1,345	KA; glass: quench growths.
		1,340	KA; C_4AF.
60	40	1,340	KA; C_4AF; trace of glass.
40	60	1,580	KA; glass.

tures. At such temperatures a certain amount of uncertainty is felt as to the accuracy of the data obtained because of the likelihood of loss of K_2O by volatilisation. Although varying amounts of K_2O are lost upon prolonged heat treatment, no dissociation of $K_2O.Al_2O_3$ was observed in the sense that there exists some definite dissociation temperature. Moreover, all of the information which may be pertinent to Portland-cement composition can be obtained from that part of the system in which the percentages of K_2O are low, because cements are low in K_2O generally.

No evidence of any compounds other than $4CaO.Al_2O_3.Fe_2O_3$ and $K_2O.Al_2O_3$ was obtained. The results indicate that the system is a binary system with one eutetic having the composition 81 per cent. of $4CaO.Al_2O_3.Fe_2O_3$ and 19 per cent. of $K_2O.Al_2O_3$. The eutetic melts at 1,343 deg. C. $\pm$ 5 deg. C. On the

$K_2O.Al_2O_3$ side of this composition the melting points rise very rapidly; the melting point of the composition containing 25 per cent. of $K_2O.Al_2O_3$ being 1,520 deg. C. $\pm$ 5 deg. C. The melting relations in this binary system are shown in *Table* 1. In addition to the data given in the table, the eutetic melting temperature and composition were checked by observing the temperature at which liquid disappeared when compositions on each side of the eutetic composition were cooled from higher temperatures. A partial temperature-concentration diagram of this system is given in *Fig.* 1 (A).

The compound $4CaO.Al_2O_3.Fe_2O_3$ apparently takes up some $K_2O.Al_2O_3$ in solid solution, inasmuch as there exists a difference in pleochroism of the $4CaO.Al_2O_3.Fe_2O_3$ grains in the absence and presence of $K_2O.Al_2O_3$. The amount of solid solution must be very limited, however, because only a slight change in the indices of refraction of the $4CaO.Al_2O_3.Fe_2O_3$ was observed. The compound

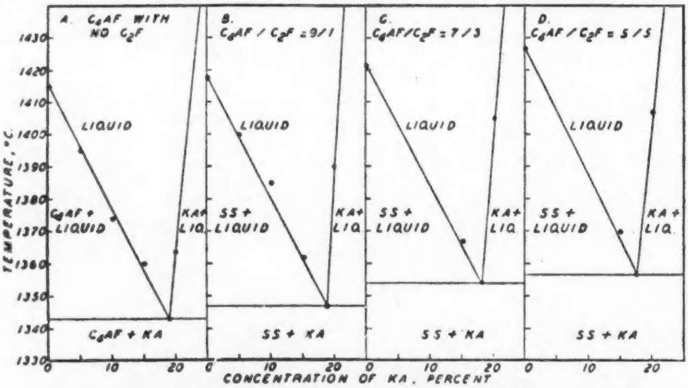

Fig. 1.—Temperature-concentration diagram showing the melting relations of C_4AF with KA and of solid solutions of C_4AF+C_2F (designated SS) with KA.

$K_2O.Al_2O_3$ likewise takes up some $4CaO.Al_2O_3.Fe_2O_3$ in solid solution. The grains of $K_2O.Al_2O_3$ containing $4CaO.Al_2O_3.Fe_2O_3$ show no birefraction, but the index of refraction has a value of 1.625 as compared with the index of 1.603, the value ascribed to the pure compound by Brownmiller [6]. It is doubtful if the amount of $4CaO.Al_2O_3.Fe_2O_3$ which goes into solution in the $K_2O.Al_2O_3$ is appreciable, because the $K_2O.Al_2O_3$ grains do not lose their isotropism. $K_2O.Al_2O_3$ was found to crystallise as colourless rounded grains, which sometimes had the appearance of octahedra. Possible further evidence of solid solution of $4CaO.Al_2O_3.Fe_2O_3$ was found in the optical properties of the $K_2O.Al_2O_3$ crystals contained in a charge of the composition 70 per cent. of $4CaO.Al_2O_3.Fe_2O_3$ and 30 per cent. of $K_2O.Al_2O_3$, which had been cooled slowly from 1,372 deg. to 1,320 deg. C. The index of the grains in general was about 1.625, but in some of the grains there were portions which appeared to have an index of about 1.61 or a trifle lower. No grains which had an index intermediate to the values 1.625

and 1.61 were observed. This would indicate that the slightest amount of solid solution is sufficient to raise the index to the maximum value of 1.625. Because the amounts of solid solution are indeterminate, the solid solutions are not indicated in *Fig.* 1 (A), and the solidus is represented by a straight line.

Relations of $4CaO.Al_2O_3.Fe_2O_3$-$2CaO.Fe_2O_3$.—Hansen, Brownmiller and Bogue [8] found that $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ form a complete series of solid solutions. The temperature-concentration diagram as constructed by them is reproduced in *Fig.* 2. Ordinarily the figure demonstrating a complete series of solid solutions consists of two curves, representing the liquidus and the solidus, respectively. In this particular case these workers found that the melting range of the solid solutions could not be determined. The heating curve method of study was employed and only one distinct break was obtained on each of the heating curves. The conclusion drawn was that the melting range of these solid solutions is very narrow, and, consequently, the temperature-concentration diagram was constructed with a single curve.

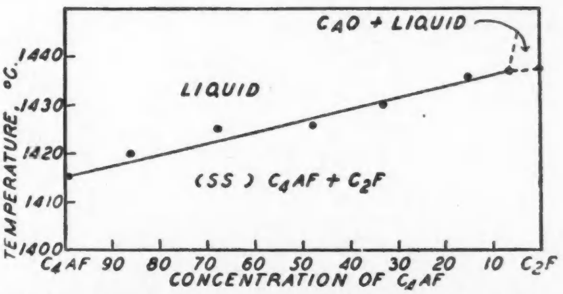

Fig. 2.—Temperature-concentration diagram showing the melting relations in the solid solution of C_4AF and C_2F.

Relations of 90 per cent. of $4CaO.Al_2O_3.Fe_2O_3$ **and 10 per cent. of** $2CaO.Fe_2O_3$-$K_2O.Al_2O_3$.—The series of compositions having the amounts of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ in the definite ratio of 9 : 1, and in which the percentage of $K_2O.Al_2O_3$ varies, cannot be considered as a true binary system, although $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ go into solid solution and separate as one phase. Strictly speaking, as the solid solution melts there exists a difference in the compositions of the liquid and the remaining solid. But, as has been mentioned, the melting range is very narrow and the difference in composition between the liquid and solid phases must necessarily be slight. Since, except for the most exacting interpretations, the relationships which obtain are similar to those of a binary system this may be referred to as forming a pseudo-binary system. (For the same reason compositions in which $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ are in some other definite ratio are treated as belonging to a pseudo-binary system in conjunction with $K_2O.Al_2O_3$.)

The composition represented by the lowest point on the liquidus curve is 81.5 per cent. of $4CaO.Al_2O_3.Fe_2O_3+2CaO.Fe_2O_3$ (73.35 per cent. of $4CaO.Al_2O_3$.

Fe_2O_3, 8.15 per cent. of $2CaO.Fe_2O_3$) and 18.5 per cent. of $K_2O.Al_2O_3$. The melting point of this mixture is 1,347 deg. C. $\pm$ 5 deg. C. The melting relations are given in *Table* 2 and the temperature-concentration diagram is shown in *Fig.* 1 (B). It will be observed that the same type of temperature-concentration relationships obtain as those which hold for the $4CaO.Al_2O_3.Fe_2O_3$—$K_2O.Al_2O_3$ system without the $2CaO.Fe_2O_3$.

The index of $K_2O.Al_2O_3$ was found to be 1.625. The birefracting iron-bearing phase had the indices α_{Li} 1.98 and γ_{Li} about 2.05. These indices agree closely with those determined by Hansen, Brownmiller, and Bogue [8] for this particular solid solution.

Relations of 70 per cent. of $4CaO.Al_2O_3.Fe_2O_3$, **30 per cent. of**

TABLE 2.—THERMAL DATA RELATIVE TO MIXTURES OF C_4AF+C_2F (9 TO 1)—KA.

Composition			Temperature of quench	Examination
C_4AF	C_2F	KA		
Percent	*Percent*	*Percent*	°*C*	
90	10	0	1,420	Quench growths; glass.
			1,415	All crystalline.
85.5	9.5	5.0	1,410	Only trace of biref. iron material, believed to be quench growths; glass.
			1,395	Solid solution C_4AF+C_2F; glass.
			1,351	Solid solution C_4AF+C_2F; glass.
			1,345	All crystalline.
81.0	9.0	10.0	1,300	Glass.
			1,385	Trace of solid solution C_4AF+CA_2F; glass.
			1 346	Trace of glass; solid solution C_4AF+C_2F; KA.
			1,343	All crystalline.
76.5	8.5	15.0	1,380	Glass.
			1,370	Do.
			1,365	Do.
			1,360	Solid solution C_4AF+C_2F; glass.
			1,355	Do.
			1,343	All crystalline.
72.0	8.0	20.0	1,390	Trace of KA; glass.
			1,380	KA; glass.
			1,370	Do.
			1,360	Do.
			1,350	Do.
67.5	7.5	25.0	1,530	Glass.
			1,520	KA; glass.
			1,354	Do.
			1,346	Trace of glass; KA; solid solution C_4AF+C_2F.

$2CaO.Fe_2O_3$—$K_2O.Al_2O_3$.—The melting points of compositions in this series are slightly higher than those of comparable compositions of the preceding series. The composition 82 per cent. of $4CaO.Al_2O_3.Fe_2O_3$ + $2CaO.Fe_2O_3$ (57.4 per cent. of $4CaO.Al_2O_3.Fe_2O_3$, 24.6 per cent. of $2CaO.Fe_2O_3$) and 18 per cent. of $K_2O.Al_2O_3$, which melts at 1,354 deg. C. $\pm$ 5 deg. C, is the lowest-melting composition. No additional compounds were observed. $K_2O.Al_2O_3$ grains retain their index of 1.625. The minimum index for lithium light of the crystalline solid solution of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ was found to be about 2.05. This value is very close to that read from the diagram constructed by Hansen, Brownmiller, and Bogue [8] in which the indices of refraction of the solid solutions are plotted against composition. The thermal relations of compositions in this pseudo-

TABLE 3.—THERMAL DATA RELATIVE TO MIXTURES OF C_4AF+C_2F (7 TO 3)—KA.

Composition			Temperature of quench	Examination
C_4AF	C_2F	KA		
Percent	*Percent*	*Percent*	°*C*	
70.0	30.0	0.0	1,425	Glass; quench growths.
			1,420	Mostly crystalline; trace of glass.
66.5	28.5	5.0	1,430	Glass; quench growths.
			1,420	Do.
			1,410	Do.
			1,362	Solid solution C_4AF+C_2F; glass.
			1,357	Solid solution C_4AF+C_2F; small amount of glass.
			1,353	Solid solution C_4AF+C_2F; KA; only trace of glass.
			1,340	All crystalline.
63.0	27.0	10.0	1,420	Glass; quench growths.
			1,410	Do.
			1,357	Solid solution C_4AF+C_2F; glass.
			1,350	All crystalline.
59.5	25.5	15.0	1,380	Glass.
			1,370	Do.
			1,365	Solid solution C_4AF+C_2F; glass.
			1,357	Solid solution C_4AF+C_2F; KA; small amount of glass.
			1,350	All crystalline.
56.0	24.0	20.0	1,410	Glass.
			1,400	KA; glass.
			1,390	Do.
52.5	22.5	25.0	1,520	Trace of KA; glass.
			1,510	KA; glass.
			1,357	Poorly defined crystals; some glass.
			1,350	All crystalline.

TABLE 4.—THERMAL DATA RELATIVE TO MIXTURES OF C_4AF+C_2F (5 TO 5)—KA.

Composition			Temperature of quench	Examination
C_4AF	C_2F	KA		
Percent 50	*Percent* 50	*Percent* 0	°*C* ----------	Melting temperature 1,427° C, according to Hansen, Brownmiller, and Bogue.
47.5	47.5	5.0	1,357	Few quench growths; mostly crystalline.[1]
45.0	45.0	10.0	1,357	Do.[1]
42.5	42.5	15.0	1,380	Glass.
			1,370	Trace solid solution C_4AF+C_2F; glass.
40.0	40.0	20.0	1,410	Glass.
			1,405	KA; glass.
			1,357	KA; some solid solution C_4AF+C_2F; trace of glass.
37.5	37.5	25.0	1,530	Glass.
			1,520	Trace KA; glass.
			1,515	Much KA; glass.

[1] Quenches of samples containing less than 15 percent of KA were very unsatisfactory.

binary system are given in *Table* 3 and the graphic interpretation is shown in *Fig.* 1 (C).

Relations of 50 per cent. of $4CaO.Al_2O_3.Fe_2O_3$, **50 per cent. of** $2CaO.Fe_2O_3$-$K_2O.Al_2O_3$.—The same relationships hold for this pseudo-binary system as for the preceding systems in which one component is composed of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ in a definite proportion. The melting points are, in general, increased as a result of the increased amount of $2CaO.Fe_2O_3$ in the solid solution. The composition of the lowest-melting composition is 82.5 per cent. of $4CaO.Al_2O_3.Fe_2O_3 + 2CaO.Fe_2O_3$ (41.25 per cent. of $4CaO.Al_2O_3.Fe_2O_3$, 41.25 per cent. of $2CaO.Fe_2O_3$) and 17.5 per cent. of $K_2O.Al_2O_3$. It melts at 1,357 deg. C. $\pm$ 5 deg. C. The data pertaining to the quenches in this

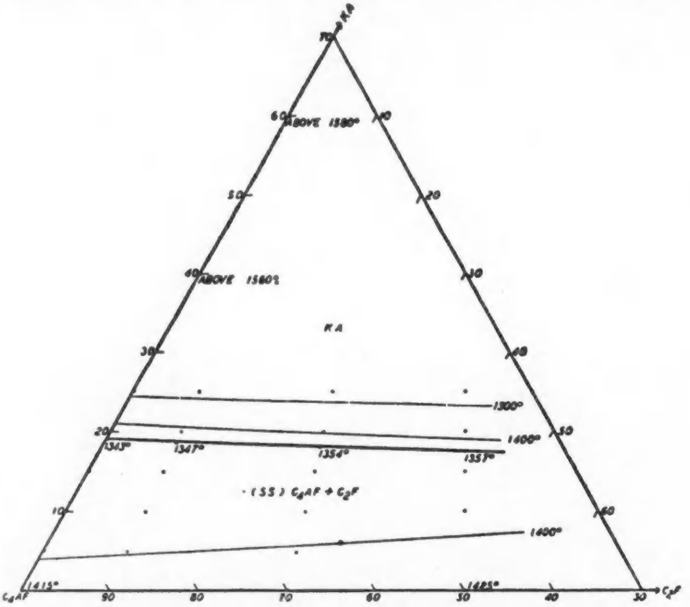

Fig. 3.—Diagram showing fields of primary crystallisation and isotherms with mixtures of C_4AF, C_2F, KA.

system are shown in *Table* 4, and the temperature-concentration diagram in *Fig.* 1 (D). The index of $K_2O.Al_2O_3$, as in the preceding systems, was 1.625. The minimum index for lithium light of the crystalline iron-bearing material was slightly less than 2.10, probably 2.08. This value, likewise, is in close agreement with that reported by Hansen, Brownmiller, and Bogue.

General Relations of $4CaO.Al_2O_3.Fe_2O_3$-$2CaO.Fe_2O_3$-$K_2O.Al_2O_3$.—No compounds of potash other than $K_2O.Al_2O_3$ were found to exist at equilibrium in the region studied. The compound $4CaO.Al_2O_3.Fe_2O_3$ is stable in the presence of $K_2O.Al_2O_3$ and forms a series of solid solutions with $2CaO.Fe_2O_3$ as it does

in the absence of $K_2O.Al_2O_3$. *Fig.* 3 shows the fields of primary crystallisation and the 1,400 deg. and 1,500 deg. C. isotherms. The boundary curve separating the field of $K_2O.Al_2O_3$ from the field of the solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ may be considered as defining the lowest-melting compositions which will exist in any mixture of $K_2O.Al_2O_3$, $4CaO.Al_2O_3.Fe2O_3$, and $2CaO.Fe_2O_3$ in which the ratio of $4CaO.Al_2O_3.Fe_2O_3$ to $2CaO.Fe_2O_3$ does not exceed 1.0 (the limit of the region studied). It will be seen that the percentage of $K_2O.Al_2O_3$ present in the lowest-melting compositions decreases slightly as the ratio of $4CaO.Al_2O_3.Fe_2O_3$ to $2CaO.Fe_2O_3$ decreases. There is a small rise in the melting temperatures of these compositions as the ratio of $4CaO.Al_2O_3.Fe_2O_3$ to $2CaO.Fe_2O_3$ decreases, as shown in *Fig.* 1. The temperatures required for complete melting of the compositions in the field in which $K_2O.Al_2O_3$ is the primary phase increase very sharply as the percentage of $K_2O.Al_2O_3$ increases.

Significance of the Study in Regard to the Constitution of Portland Cement.

Although the alkalis generally are referred to as being among the minor constituents of Portland cement clinker, it is recognised that K_2O and Na_2O

TABLE 5.—THE EFFECT OF VARYING AMOUNTS OF K_2O ON THE COMBINATION OF CaO AT A DEFINITE TEMPERATURE.

Percentage composition of mixture					Burning temperature	Free CaO
CaO	K_2O	Al_2O_3	Fe_2O_3	SiO_2		
					°C	Percent
67.0	0.0	7.5	2.5	23.0	1,450	1.1
66.5	.5	7.5	2.5	23.0	1,450	.5
66.0	1.0	7.5	2.5	23.0	1,450	1.6
65.0	2.0	7.5	2.5	23.0	1,450	4.3
64.0	3.0	7.5	2.5	23.0	1,450	7.3

may combine with other oxides present in such a manner as to be of great effect in determining the ultimate composition. It was found in a study of the influence of K_2O on the burnability of cement compositions in this laboratory [9] that, although the first small increments of K_2O favoured combination, higher free-lime values obtained in clinkers burned at a definite temperature as K_2O was substituted for like percentages of CaO beyond an optimum value. This optimum amount was found to vary with the composition of the base mixture, but generally was less than 1 per cent. A typical example is given in *Table* 5.

The manner in which K_2O is combined in Portland cement clinker is to be established by a series of phase-equilibria studies involving K_2O and the other constituents. The results of Brownmiller's investigation of the system $CaO–K_2O–Al_2O_3$ show that $K_2O.Al_2O_3$ is the only compound of K_2O in that system which exists in compositions related to Portland cement compositions. This study shows that $K_2O.Al_2O_3$ likewise is stable in the presence of $4CaO.Al_2O_3.Fe_2O_3$. Furthermore, the compound $K_2O.Al_2O_3$ can exist in the presence of $2CaO.Fe_2O_3$, which may be present in rare instances in cements having an $Al_2O_3 : Fe_2O_3$ ratio less than 0.64.

Phase equilibria studies on mixtures of $K_2O.Al_2O_3$ and the other constituents of cement clinker necessarily follow. If such studies indicate that $K_2O.Al_2O_3$ is stable in the presence of $3CaO.SiO_2$ and $2CaO.SiO_2$, then it may be that $K_2O.Al_2O_3$ exists in clinker. On the other hand, if $K_2O.Al_2O_3$ reacts with any of these compounds to form a new combination, such as xCaO.yK$_2$O.zSiO$_2$ or xK$_2$O.ySiO$_2$, then it will be necessary to study the relations of that combination with the various cement constituents $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, etc.

In view of recent discoveries by Insley and McMurdie [10], the latter condition appears to be likely. With the development of the technique for examining polished sections of clinkers in reflected light, these workers have observed a dark prismatic interstitial material in many commercial cement clinkers. It was found that this material did not occur in alkali-free laboratory preparations, but did exist if either or both Na_2O and K_2O were present. The mean refractive index of this weakly birefracting phase was found to be near 1.72. No crystals possessing optical properties similar to those of $K_2O.Al_2O_3$ were observed.

Although the treatment in this paper has been concerned exclusively with equilibrium crystallisation of the phases studied, clinker contains varying amounts of glass and this glass may contain a part or all of the alkali components. The degree of crystallisation of the alkali phases at any temperature can only be determined through further study of the course of crystallisation now in progress.

REFERENCES.

[1] L. T. Brownmiller and R. H. Bogue, BS J. Research **5**, 813 (1930) RP233; Am, J. Sci. **20**, 241 (1930).
[2] F. M. Lea and T. W. Parker, Bldg. Research Tech. Pap. 16 (1935).
[3] L. A. Dahl, Rock Products **35**, No. 12, 31 (1932).
[4] H. F. McMurdie and H. Insley, J. Research NBS **16**, 467 (1936) RP884.
[5] L. T. Brownmiller and R. H. Bogue, BS J. Research **8**, 289 (1932) RP414; Am. J. Sci. **23**, 501 (1932).
[6] L. T. Brownmiller, Am. J. Sci. **29**, 260 (1935).
[7] Adams, J. Opt. Soc. Am. **9**, 599 (1924).
[8] W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, J. Am. Chem. Soc. **50**, 396 (1928)
[9] W. C. Taylor, Unpublished data.
[10] H. Insley and H. F. McMurdie, J. Research NBS **20**, 173 (1938) RP1074.